

OXFORD



ATKINS'
PHYSICAL
CHEMISTRY

twelfth edition

PETER ATKINS | JULIO DE PAULA | JAMES KEELER



Enhanced E-book

Useful relations

At 298.15 K

RT	2.4790 kJ mol ⁻¹	RT/F	25.693 mV
$(RT/F) \ln 10$	59.160 mV	kT/hc	207.225 cm ⁻¹
kT	25.693 meV	V_m^\ominus	2.4790 × 10 ⁻² m ³ mol ⁻¹ 24.790 dm ³ mol ⁻¹

Selected units*

1 N	1 kg m s ⁻²	1 J	1 kg m ² s ⁻²
1 Pa	1 kg m ⁻¹ s ⁻²	1 W	1 J s ⁻¹
1 V	1 J C ⁻¹	1 A	1 C s ⁻¹
1 T	1 kg s ⁻² A ⁻¹	1 P	10 ⁻¹ kg m ⁻¹ s ⁻¹
1 S	1 Ω ⁻¹ = 1 A V ⁻¹		

* For multiples (milli, mega, etc), see the Resource section

Conversion factors

$$\theta/^{\circ}\text{C} = T/\text{K} - 273.15^*$$

1 eV	1.602 177 × 10 ⁻¹⁹ J	1 cal	4.184* J
	96.485 kJ mol ⁻¹		
	8065.5 cm ⁻¹		
1 atm	101.325* kPa	1 cm ⁻¹	1.9864 × 10 ⁻²³ J
	760* Torr		
1 D	3.335 64 × 10 ⁻³⁰ C m	1 Å	10 ⁻¹⁰ m*

* Exact value

Mathematical relations

$$\pi = 3.141\,592\,653\,59 \dots \quad e = 2.718\,281\,828\,46 \dots$$

Logarithms and exponentials

$$\begin{aligned} \ln x + \ln y + \dots &= \ln xy \dots & \ln x - \ln y &= \ln(x/y) \\ a \ln x &= \ln x^a & \ln x &= (\ln 10) \log x \\ & & &= (2.302\,585 \dots) \log x \\ e^x e^y e^z \dots &= e^{x+y+z+\dots} & e^x/e^y &= e^{x-y} \\ (e^x)^a &= e^{ax} & e^{\pm ix} &= \cos x \pm i \sin x \end{aligned}$$

Series expansions

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots$$

$$\frac{1}{1+x} = 1 - x + x^2 - \dots \quad \frac{1}{1-x} = 1 + x + x^2 + \dots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \dots \quad \cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \dots$$

Derivatives; for Integrals, see the Resource section

$$d(f+g) = df + dg \quad d(fg) = f dg + g df$$

$$d\frac{f}{g} = \frac{1}{g} df - \frac{f}{g^2} dg \quad \frac{df}{dt} = \frac{df}{dg} \frac{dg}{dt} \quad \text{for } f = f(g(t))$$

$$\left(\frac{\partial y}{\partial x}\right)_z = 1 / \left(\frac{\partial x}{\partial y}\right)_z \quad \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$$

$$\frac{dx^n}{dx} = nx^{n-1} \quad \frac{de^{ax}}{dx} = ae^{ax} \quad \frac{d \ln(ax)}{dx} = \frac{1}{x}$$

$$df = g(x, y)dx + h(x, y)dy \text{ is exact if } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

Greek alphabet*

A, α	alpha	I, ι	iota	P, ρ	rho
B, β	beta	K, κ	kappa	Σ, σ	sigma
Γ, γ	gamma	Λ, λ	lambda	T, τ	tau
Δ, δ	delta	M, μ	mu	Υ, υ	upsilon
E, ε	epsilon	N, ν	nu	Φ, φ	phi
Z, ζ	zeta	Ξ, ξ	xi	X, χ	chi
H, η	eta	O, o	omicron	Ψ, ψ	psi
Θ, θ	theta	Π, π	pi	Ω, ω	omega

* Oblique versions (α, β, ...) are used to denote physical observables.

PERIODIC TABLE OF THE ELEMENTS

		Period 1																18	
Group		1	2											13	14	15	16	17	2
		I	II											III	IV	V	VI	VII	VIII
		IA	IIA											IIIA	IVA	VA	VIA	VIIA	VIIA
		1 H hydrogen 1.0079 1s ¹																2 He helium 4.00 1s ²	
2		3 Li lithium 6.94 2s ¹	4 Be beryllium 9.01 2s ²											5 B boron 10.81 2s ² 2p ¹	6 C carbon 12.01 2s ² 2p ²	7 N nitrogen 14.01 2s ² 2p ³	8 O oxygen 16.00 2s ² 2p ⁴	9 F fluorine 19.00 2s ² 2p ⁵	10 Ne neon 20.18 2s ² 2p ⁶
3		11 Na sodium 22.99 3s ¹	12 Mg magnesium 24.31 3s ²											13 Al aluminium 26.98 3s ² 3p ¹	14 Si silicon 28.09 3s ² 3p ²	15 P phosphorus 30.97 3s ² 3p ³	16 S sulfur 32.06 3s ² 3p ⁴	17 Cl chlorine 35.45 3s ² 3p ⁵	18 Ar argon 39.95 3s ² 3p ⁶
4		19 K potassium 39.10 4s ¹	20 Ca calcium 40.08 4s ²	21 Sc scandium 44.96 3d ¹ 4s ²	22 Ti titanium 47.87 3d ² 4s ²	23 V vanadium 50.94 3d ³ 4s ²	24 Cr chromium 52.00 3d ⁵ 4s ¹	25 Mn manganese 54.94 3d ⁵ 4s ²	26 Fe iron 55.84 3d ⁶ 4s ²	27 Co cobalt 58.93 3d ⁷ 4s ²	28 Ni nickel 58.69 3d ⁸ 4s ²	29 Cu copper 63.55 3d ¹⁰ 4s ¹	30 Zn zinc 65.41 3d ¹⁰ 4s ²	31 Ga gallium 69.72 4s ² 4p ¹	32 Ge germanium 72.64 4s ² 4p ²	33 As arsenic 74.92 4s ² 4p ³	34 Se selenium 78.96 4s ² 4p ⁴	35 Br bromine 79.90 4s ² 4p ⁵	36 Kr krypton 83.80 4s ² 4p ⁶
		3	4	5	6	7	8	9	10	11	12								
5		37 Rb rubidium 85.47 5s ¹	38 Sr strontium 87.62 5s ²	39 Y yttrium 88.91 4d ¹ 5s ²	40 Zr zirconium 91.22 4d ² 5s ²	41 Nb niobium 92.91 4d ⁴ 5s ¹	42 Mo molybdenum 95.94 4d ⁵ 5s ¹	43 Tc technetium (98) 4d ⁵ 5s ²	44 Ru ruthenium 101.07 4d ⁷ 5s ¹	45 Rh rhodium 102.90 4d ⁸ 5s ¹	46 Pd palladium 106.42 4d ¹⁰	47 Ag silver 107.87 4d ¹⁰ 5s ¹	48 Cd cadmium 112.41 4d ¹⁰ 5s ²	49 In indium 114.82 5s ² 5p ¹	50 Sn tin 118.71 5s ² 5p ²	51 Sb antimony 121.76 5s ² 5p ³	52 Te tellurium 127.60 5s ² 5p ⁴	53 I iodine 126.90 5s ² 5p ⁵	54 Xe xenon 131.29 5s ² 5p ⁶
6		55 Cs caesium 132.91 6s ¹	56 Ba barium 137.33 6s ²	57 La lanthanum	72 Hf hafnium 178.49 5d ² 6s ²	73 Ta tantalum 180.95 5d ³ 6s ²	74 W tungsten 183.84 5d ⁴ 6s ²	75 Re rhenium 186.21 5d ⁵ 6s ²	76 Os osmium 190.23 5d ⁶ 6s ²	77 Ir iridium 192.22 5d ⁷ 6s ²	78 Pt platinum 195.08 5d ⁹ 6s ¹	79 Au gold 196.97 5d ¹⁰ 6s ¹	80 Hg mercury 200.59 5d ¹⁰ 6s ²	81 Tl thallium 204.38 6s ² 6p ¹	82 Pb lead 207.2 6s ² 6p ²	83 Bi bismuth 208.98 6s ² 6p ³	84 Po polonium (209) 6s ² 6p ⁴	85 At astatine (210) 6s ² 6p ⁵	86 Rn radon (222) 6s ² 6p ⁶
7		87 Fr francium (223) 7s ¹	88 Ra radium (226) 7s ²	89 Ac actinium (227) 6d ¹ 7s ²	104 Rf rutherfordium (261) 6d ² 7s ²	105 Db dubnium (262) 6d ³ 7s ²	106 Sg seaborgium (263) 6d ⁴ 7s ²	107 Bh bohrium (262) 6d ⁵ 7s ²	108 Hs hassium (265) 6d ⁶ 7s ²	109 Mt meitnerium (266) 6d ⁷ 7s ²	110 Ds darmstadtium (271) 6d ⁸ 7s ²	111 Rg roentgenium (272) 6d ⁹ 7s ²	112 Cn copernicium ? 6d ¹⁰ 7s ²	113 Nh nihonium ? 7s ² 7p ¹	114 Fl flerovium ? 7s ² 7p ²	115 Mc moscovium ? 7s ² 7p ³	116 Lv livermorium ? 7s ² 7p ⁴	117 Ts tennessine ? 7s ² 7p ⁵	118 Og oganeson ? 7s ² 7p ⁶
6		58 Ce cerium 140.12 4f ¹ 5d ¹ 6s ²	59 Pr praseodymium 140.91 4f ³ 6s ²	60 Nd neodymium 144.24 4f ⁴ 6s ²	61 Pm promethium (145) 4f ⁵ 6s ²	62 Sm samarium 150.36 4f ⁶ 6s ²	63 Eu europium 151.96 4f ⁷ 6s ²	64 Gd gadolinium 157.25 4f ⁷ 5d ¹ 6s ²	65 Tb terbium 158.93 4f ⁹ 6s ²	66 Dy dysprosium 162.50 4f ¹⁰ 6s ²	67 Ho holmium 164.93 4f ¹¹ 6s ²	68 Er erbium 167.26 4f ¹² 6s ²	69 Tm thulium 168.93 4f ¹³ 6s ²	70 Yb ytterbium 173.04 4f ¹⁴ 6s ²	71 Lu lutetium 174.97 5d ¹ 6s ²	Lanthanoids (lanthanides)			
7		90 Th thorium 232.04 6d ² 7s ²	91 Pa protactinium 231.04 5f ² 6d ¹ 7s ²	92 U uranium 238.03 5f ³ 6d ¹ 7s ²	93 Np neptunium (237) 5f ⁴ 6d ¹ 7s ²	94 Pu plutonium (244) 5f ⁶ 7s ²	95 Am americium (243) 5f ⁷ 7s ²	96 Cm curium (247) 5f ⁷ 6d ¹ 7s ²	97 Bk berkelium (247) 5f ⁹ 7s ²	98 Cf californium (251) 5f ¹⁰ 7s ²	99 Es einsteinium (252) 5f ¹¹ 7s ²	100 Fm fermium (257) 5f ¹² 7s ²	101 Md mendelevium (258) 5f ¹³ 7s ²	102 No nobelium (259) 5f ¹⁴ 7s ²	103 Lr lawrencium (262) 6d ¹ 7s ²	Actinoids (actinides)			

Numerical values of molar masses in grams per mole (atomic weights) are quoted to the number of significant figures typical of most naturally occurring samples.

FUNDAMENTAL CONSTANTS

Constant	Symbol	Value		
			Power of 10	Units
Speed of light	c	2.997 924 58*	10 ⁸	m s ⁻¹
Elementary charge	e	1.602 176 634*	10 ⁻¹⁹	C
Planck's constant	h	6.626 070 15	10 ⁻³⁴	J s
	$\hbar = h/2\pi$	1.054 571 817	10 ⁻³⁴	J s
Boltzmann's constant	k	1.380 649*	10 ⁻²³	JK ⁻¹
Avogadro's constant	N_A	6.022 140 76	10 ²³	mol ⁻¹
Gas constant	$R = N_A k$	8.314 462		JK ⁻¹ mol ⁻¹
Faraday's constant	$F = N_A e$	9.648 533 21	10 ⁴	C mol ⁻¹
Mass				
Electron	m_e	9.109 383 70	10 ⁻³¹	kg
Proton	m_p	1.672 621 924	10 ⁻²⁷	kg
Neutron	m_n	1.674 927 498	10 ⁻²⁷	kg
Atomic mass constant	m_u	1.660 539 067	10 ⁻²⁷	kg
Magnetic constant (vacuum permeability)	μ_0	1.256 637 062	10 ⁻⁶	J s ² C ⁻² m ⁻¹
Electric constant (vacuum permittivity)	$\epsilon_0 = 1/\mu_0 c^2$	8.854 187 813	10 ⁻¹²	J ⁻¹ C ² m ⁻¹
	$4\pi\epsilon_0$	1.112 650 056	10 ⁻¹⁰	J ⁻¹ C ² m ⁻¹
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 010 08	10 ⁻²⁴	J T ⁻¹
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 783 75	10 ⁻²⁷	J T ⁻¹
Proton magnetic moment	μ_p	1.410 606 797	10 ⁻²⁶	J T ⁻¹
g -Value of electron	g_e	2.002 319 304		
Magnetogyric ratio				
Electron	$\gamma_e = g_e e/2m_e$	1.760 859 630	10 ¹¹	T ⁻¹ s ⁻¹
Proton	$\gamma_p = 2\mu_p/\hbar$	2.675 221 674	10 ⁸	T ⁻¹ s ⁻¹
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/e^2m_e$	5.291 772 109	10 ⁻¹¹	m
Rydberg constant	$\tilde{R}_\infty = m_e e^4/8h^3 c\epsilon_0^2$	1.097 373 157	10 ⁵	cm ⁻¹
	$hc\tilde{R}_\infty/e$	13.605 693 12		eV
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 352 5693	10 ⁻³	
	α^{-1}	1.370 359 999 08	10 ²	
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 374	10 ⁻⁸	W m ⁻² K ⁻⁴
Standard acceleration of free fall	g	9.806 65*		m s ⁻²
Gravitational constant	G	6.674 30	10 ⁻¹¹	N m ² kg ⁻²

* Exact value. For current values of the constants, see the National Institute of Standards and Technology (NIST) website.

Atkins'

PHYSICAL CHEMISTRY

Twelfth edition

Peter Atkins

Fellow of Lincoln College,
University of Oxford,
Oxford, UK

Julio de Paula

Professor of Chemistry,
Lewis & Clark College,
Portland, Oregon, USA

James Keeler

Associate Professor of Chemistry,
University of Cambridge, and
Walters Fellow in Chemistry at Selwyn College,
Cambridge, UK

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PREFACE

Our *Physical Chemistry* is continuously evolving in response to users' comments, our own imagination, and technical innovation. The text is mature, but it has been given a new vibrancy: it has become dynamic by the creation of an e-book version with the pedagogical features that you would expect. They include the ability to summon up living graphs, get mathematical assistance in an awkward derivation, find solutions to exercises, get feedback on a multiple-choice quiz, and have easy access to data and more detailed information about a variety of subjects. These innovations are not there simply because it is now possible to implement them: they are there to help students at every stage of their course.

The flexible, popular, and less daunting arrangement of the text into readily selectable and digestible Topics grouped together into conceptually related Focuses has been retained. There have been various modifications of emphasis to match the evolving subject and to clarify arguments either in the light of readers' comments or as a result of discussion among ourselves. We learn as we revise, and pass on that learning to our readers.

Our own teaching experience ceaselessly reminds us that mathematics is the most fearsome part of physical chemistry, and we likewise ceaselessly wrestle with finding ways to overcome that fear. First, there is encouragement to use mathematics, for it is the language of much of physical chemistry. The *How is that done?* sections are designed to show that if you want to make progress with a concept, typically making it precise and quantitative, then you have to deploy mathematics. Mathematics opens doors to progress. Then there is the fine-grained help with the manipulation of equations, with their detailed annotations to indicate the steps being taken.

Behind all that are *The chemist's toolkits*, which provide brief reminders of the underlying mathematical techniques. There is more behind them, for the collections of Toolkits available via the e-book take their content further and provide illustrations of how the material is used.

The text covers a very wide area and we have sought to add another dimension: depth. Material that we judge too detailed for the text itself but which provides this depth of treatment, or simply adds material of interest springing from the introductory material in the text, can now be found in enhanced *A deeper look* sections available via the e-book. These sections are there for students and instructors who wish to extend their knowledge and see the details of more advanced calculations.

The main text retains *Examples* (where we guide the reader through the process of answering a question) and *Brief illustrations* (which simply indicate the result of using an equation, giving a sense of how it and its units are used). In this edition a few Exercises are provided at the end of each major section in a Topic along with, in the e-book, a selection of multiple-choice questions. These questions give the student the opportunity to check their understanding, and, in the case of the e-book, receive immediate feedback on their answers. Straightforward Exercises and more demanding Problems appear at the end of each Focus, as in previous editions.

The text is living and evolving. As such, it depends very much on input from users throughout the world. We welcome your advice and comments.

PWA
JdeP
JK

USING THE BOOK

TO THE STUDENT

The twelfth edition of *Atkins' Physical Chemistry* has been developed in collaboration with current students of physical chemistry in order to meet your needs better than ever before. Our student reviewers have helped us to revise our writing style to retain clarity but match the way you read. We have also introduced a new opening section, *Energy: A first look*, which summarizes some key concepts that are used throughout the text and are best kept in mind right from the beginning. They are all revisited in greater detail later. The new edition also brings with it a hugely expanded range of digital resources, including living graphs, where you can explore the consequences of changing parameters, video interviews with practising scientists, video tutorials that help to bring key equations to life in each Focus, and a suite of self-check questions. These features are provided as part of an enhanced e-book, which is accessible by using the access code included in the book.

You will find that the e-book offers a rich, dynamic learning experience. The digital enhancements have been crafted to help your study and assess how well you have understood the material. For instance, it provides assessment materials that give you regular opportunities to test your understanding.

Innovative structure

Short, selectable Topics are grouped into overarching Focus sections. The former make the subject accessible; the latter provides its intellectual integrity. Each Topic opens with the questions that are commonly asked: why is this material important?, what should you look out for as a key idea?, and what do you need to know already?

Resource section

The *Resource section* at the end of the book includes a brief review of two mathematical tools that are used throughout the text: differentiation and integration, including a table of the integrals that are encountered in the text. There is a review of units, and how to use them, an extensive compilation of tables of physical and chemical data, and a set of character tables. Short extracts of most of these tables appear in the Topics themselves: they are there to give you an idea of the typical values of the physical quantities mentioned in the text.

FOCUS 5 SIMPLE MIXTURES

Peter Atkins
School of Chemistry, University of Oxford, Oxford, UK
Julio de Paula
Professor of Chemistry, Lewis & Clark College, Portland, Oregon, USA
Janine Kozisek
Honorary Professor of Chemistry, University of Cambridge, and Honorary Fellow in Chemistry at Queens College, Cambridge, UK

Students are an essential part of chemistry, often in their own right as well as starting materials for chemical reactions. This group of Topics deals with the physical properties of mixtures and shows how to express them in terms of thermodynamic quantities.

5A The thermodynamic description of mixtures

The first Topic in this Focus develops the concept of chemical potential as an example of a partial molar quantity and explains how the chemical potential of a substance is used to describe the physical properties of mixtures. The key idea is that at equilibrium the chemical potential of a species is the same in every phase. By making use of the experimental observations known as Raoult's and Henry's laws, it is possible to express the chemical potential of a substance in terms of its mole fraction in a mixture.

5A.1 Partial molar quantities 5A.2 The thermodynamics of mixing 5A.3 The chemical potentials of liquids

5B The properties of solutions

In this Topic, the concept of chemical potential is applied to the derivation of the effect of a solute on certain properties of a solution. These properties include the lowering of the vapour pressure of the solvent, the elevation of its boiling point, the depression of its freezing point, and the change of osmotic pressure. It is possible to construct a model of a certain class of non-ideal solutions called regular solutions, which have properties that diverge from those of ideal solutions.

5B.1 Liquid mixtures 5B.2 Colloidal systems

AVAILABLE IN THE E-BOOK

'Impact on...' sections

'Impact on' sections show how physical chemistry is applied in a variety of modern contexts. They showcase physical chemistry as an evolving subject.

Go to this location in the accompanying e-book to view a list of Impacts.

Group theory tables

A link to comprehensive group theory tables can be found at the end of the accompanying e-book.

The chemist's toolkits

The chemist's toolkits are reminders of the key mathematical, physical, and chemical concepts that you need to understand in order to follow the text.

For a consolidated and enhanced collection of the toolkits found throughout the text, go to this location in the accompanying e-book.

'A deeper look' sections

These sections take some of the material in the text further and are there if you want to extend your knowledge and see the details of some of the more advanced derivations.

Go to this location in the accompanying e-book to view a list of Deeper Looks.

TOPIC 2A Internal energy

Why do you need to know this material?

The First Law of thermodynamics is the foundation of the discussion of the role of energy in chemistry. Wherever the generation or use of energy in physical transformations or chemical reactions is of interest, lying in the background are the concepts introduced by the First Law.

What is the key idea?

The total energy of an isolated system is constant.

What do you need to know already?

This Topic makes use of the discussion of the properties of gases (Topic 1A), particularly the perfect gas law. It builds on the definition of work given in *Energy: A first look*.

A closed system has a boundary through which matter cannot be transferred.

Both open and closed systems can exchange energy with their surroundings.

An isolated system can exchange neither energy nor matter with its surroundings.

2A.1 Work, heat, and energy

Although thermodynamics deals with the properties of bulk systems, it is enriched by understanding the molecular origins of these properties. What follows are descriptions of work, heat, and energy from both points of view.

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Checklist of concepts

A checklist of key concepts is provided at the end of each Topic, so that you can tick off the ones you have mastered.

Physical chemistry: people and perspectives

Leading figures in a variety of fields share their unique and varied experiences and careers, and talk about the challenges they faced and their achievements to give you a sense of where the study of physical chemistry can lead.

PRESENTING THE MATHEMATICS

How is that done?

You need to understand how an equation is derived from reasonable assumptions and the details of the steps involved. This is one role for the *How is that done?* sections. Each one leads from an issue that arises in the text, develops the necessary equations, and arrives at a conclusion. These sections maintain the separation of the equation and its derivation so that you can find them easily for review, but at the same time emphasize that mathematics is an essential feature of physical chemistry.

The chemist's toolkits

The *chemist's toolkits* are reminders of the key mathematical, physical, and chemical concepts that you need to understand in order to follow the text. Many of these Toolkits are relevant to more than one Topic, and you can view a compilation of them, with enhancements in the form of more information and brief illustrations, in this section of the accompanying e-book.

Annotated equations and equation labels

We have annotated many equations to help you follow how they are developed. An annotation can help you travel across the equals sign: it is a reminder of the substitution used, an approximation made, the terms that have been assumed constant, an integral used, and so on. An annotation can also be a reminder of the significance of an individual term in an expression. We sometimes collect into a small box a collection of numbers or symbols to show how they carry from one line to the next. Many of the equations are labelled to highlight their significance.

Checklist of concepts

- 1. **Work** is the process of achieving motion against an opposing force.
- 2. **Energy** is the capacity to do work.
- 3. **Heat** is the process of transferring energy as a result of



Physical Chemistry: People and Perspectives

Interview with Sean M. Decatur
President of Kenyon College

How is that done? 2B.1 Deriving the relation between enthalpy change and heat transfer at constant pressure

In a typical thermodynamic derivation, as here, a common way to proceed is to introduce successive definitions of the quantities of interest and then apply the appropriate constraints.

Step 1 Write an expression for $H + dH$ in terms of the definition of H

For a general infinitesimal change in the state of the system, U changes to $U + dU$, p changes to $p + dp$, and V changes to

The chemist's toolkit 7B.1 Complex numbers

A complex number z has the form $z = x + iy$, where $i = \sqrt{-1}$. The complex conjugate of a complex number z is $z^* = x - iy$. Complex numbers combine together according to the following rules:

Addition and subtraction:

$$(a + ib) + (c + id) = (a + c) + i(b + d)$$

$$\begin{aligned} \ln \mathcal{W} &= \ln \frac{N!}{N_0! N_1! N_2! \dots} = \ln N! - \ln(N_0! N_1! N_2! \dots) \\ &= \ln N! - \ln N_0! - \ln N_1! - \ln N_2! - \dots = \ln N! - \sum_i \ln N_i! \end{aligned}$$

ln(xy) = ln x + ln y
ln(xy) = ln x - ln y

Checklists of equations

A handy checklist at the end of each topic summarizes the most important equations and the conditions under which they apply. Don't think, however, that you have to memorize every equation in these checklists: they are collected there for ready reference.

Video tutorials on key equations

Video tutorials to accompany each Focus dig deeper into some of the key equations used throughout that Focus, emphasizing the significance of an equation, and highlighting connections with material elsewhere in the book.

Living graphs

The educational value of many graphs can be heightened by seeing—in a very direct way—how relevant parameters, such as temperature or pressure, affect the plot. You can now interact with key graphs throughout the text in order to explore how they respond as the parameters are changed. These graphs are clearly flagged throughout the book, and you can find links to the dynamic versions in the corresponding location in the e-book.

SETTING UP AND SOLVING PROBLEMS

Brief illustrations

A *Brief illustration* shows you how to use an equation or concept that has just been introduced in the text. It shows you how to use data and manipulate units correctly. It also helps you to become familiar with the magnitudes of quantities.

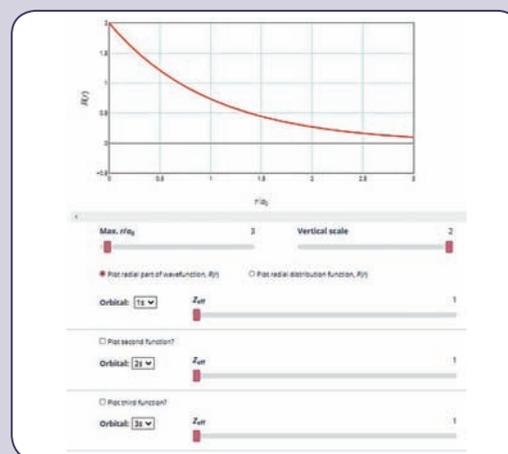
Examples

Worked *Examples* are more detailed illustrations of the application of the material, and typically require you to assemble and deploy several relevant concepts and equations.

Everyone has a different way to approach solving a problem, and it changes with experience. To help in this process, we suggest how you should collect your thoughts and then proceed to a solution. All the worked *Examples* are accompanied by closely related self-tests to enable you to test your grasp of the material after working through our solution as set out in the *Example*.

Checklist of equations

Property	Equation
Enthalpy	$H = U + pV$
Heat transfer at constant pressure	$dH = dq_p$, $\Delta H = q_p$



Brief illustration 2B.2

In the reaction $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$, 4 mol of gas-phase molecules is replaced by 2 mol of gas-phase molecules, so $\Delta n_g = -2$ mol. Therefore, at 298 K, when $RT = 2.5 \text{ kJ mol}^{-1}$, the molar enthalpy and molar internal energy changes taking place in the system are related by

Example 2B.2 Evaluating an increase in enthalpy with temperature

What is the change in molar enthalpy of N_2 when it is heated from 25 °C to 100 °C? Use the heat capacity information in Table 2B.1.

Collect your thoughts The heat capacity of N_2 changes with temperature significantly in this range, so use eqn 2B.9.

The solution Using $a = 28.58 \text{ J K}^{-1} \text{ mol}^{-1}$, $b = 3.77 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$,

Self-check questions

This edition introduces self-check questions throughout the text, which can be found at the end of most sections in the e-book. They test your comprehension of the concepts discussed in each section, and provide instant feedback to help you monitor your progress and reinforce your learning. Some of the questions are multiple choice; for them the 'wrong' answers are not simply random numbers but the result of errors that, in our experience, students often make. The feedback from the multiple choice questions not only explains the correct method, but also points out the mistakes that led to the incorrect answer. By working through the multiple-choice questions you will be well prepared to tackle more challenging exercises and problems.

Discussion questions

Discussion questions appear at the end of each Focus, and are organized by Topic. They are designed to encourage you to reflect on the material you have just read, to review the key concepts, and sometimes to think about its implications and limitations.

Exercises and problems

Exercises are provided throughout the main text and, along with Problems, at the end of every Focus. They are all organized by Topic. Exercises are designed as relatively straightforward numerical tests; the Problems are more challenging and typically involve constructing a more detailed answer. For this new edition, detailed solutions are provided in the e-book in the same location as they appear in print.

For the Examples and Problems at the end of each Focus detailed solutions to the odd-numbered questions are provided in the e-book; solutions to the even-numbered questions are available only to lecturers.

Integrated activities

At the end of every Focus you will find questions that span several Topics. They are designed to help you use your knowledge creatively in a variety of ways.

FOCUS 1 The properties of gases

To test your understanding of this material, work through the Exercises, Additional exercises, Discussion questions, and Problems found throughout this Focus.

Selected solutions can be found at the end of this Focus in the e-book. Solutions to even-numbered questions are available online only to lecturers.

TOPIC 1A The perfect gas

Discussion questions

D1A.1 Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's law, and Avogadro's principle.

D1A.2 Explain the term 'partial pressure' and explain why Dalton's law is a limiting law.

Additional exercises

E1A.8 Express (i) 22.5 kPa in atmospheres and (ii) 770 Torr in pascals.

E1A.9 Could 25 g of argon gas in a vessel of volume 1.5 dm³ exert a pressure of 2.0 bar at 30 °C if it behaved as a perfect gas? If not, what pressure would it exert?

E1A.10 A perfect gas undergoes isothermal expansion, which increases its volume by 2.20 dm³. The final pressure and volume of the gas are 5.04 bar and 4.65 dm³, respectively. Calculate the original pressure of the gas in (i) bar, (ii) atm.

E1A.11 A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 dm³. The final pressure and volume of the gas are 1.97 bar and 2.14 dm³, respectively. Calculate the original pressure of the gas in (i) bar, (ii) torr.

E1A.12 A car tyre (an automobile tyre) was inflated to a pressure of 24 lb/in² (1.00 atm = 14.7 lb/in²) on a winter's day when the temperature was -9 °C. What pressure will be found, assuming no leaks have occurred and that the volume is constant, on a subsequent summer's day when the temperature is 35 °C? What complications should be taken into account in practice?

E1A.13 A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23 °C. What can its pressure be expected to be when the temperature is 11 °C?

E1A.14 A sample of 255 mg of neon occupies 3.00 dm³ at 122 K. Use the perfect gas law to calculate the pressure of the gas.

E1A.15 A homeowner uses 4.00 × 10³ m³ of natural gas in a year to heat a home. Assume that natural gas is all methane, CH₄, and that methane is a perfect gas for the conditions of this problem, which are 1.00 atm and 20 °C. What is the mass of gas used?

E1A.16 At 100 °C and 16.0 kPa, the mass density of phosphorus vapour is 0.6388 kg m⁻³. What is the molecular formula of phosphorus under these conditions?

E1A.17 Calculate the mass of water vapour present in a room of volume 400 m³ that contains air at 27 °C on a day when the relative humidity is

60 per cent. *Hint:* Relative humidity is the prevailing partial pressure of water vapour expressed as a percentage of the vapour pressure of water at the same temperature (in this case, 35.6 mbar).

E1A.18 Calculate the mass of water vapour present in a room of volume 250 m³ that contains air at 23 °C on a day when the relative humidity is 53 per cent (in this case, 28.1 mbar).

E1A.19 Given that the mass density of air at 0.987 bar and 27 °C is 1.146 kg m⁻³, calculate the mole fraction and partial pressure of nitrogen and oxygen assuming that (i) air consists only of these two gases, (ii) air also contains 1.0 mole per cent Ar.

E1A.20 A gas mixture consists of 320 mg of methane, 175 mg of argon, and 225 mg of neon. The partial pressure of neon at 300 K is 8.87 kPa. Calculate (i) the volume and (ii) the total pressure of the mixture.

E1A.21 The mass density of a gaseous compound was found to be 1.23 kg m⁻³ at 330 K and 20 kPa. What is the molar mass of the compound?

E1A.22 In an experiment to measure the molar mass of a gas, 250 cm³ of the gas was confined in a glass vessel. The pressure was 152 Torr at 298 K, and after correcting for buoyancy effects, the mass of the gas was 33.5 mg. What is the molar mass of the gas?

E1A.23 The densities of air at -85 °C, 0 °C, and 100 °C are 1.877 g dm⁻³, 1.294 g dm⁻³, and 0.946 g dm⁻³, respectively. From these data, and assuming that air obeys Charles's law, determine a value for the absolute zero of temperature in degrees Celsius.

E1A.24 A certain sample of a gas has a volume of 20.00 dm³ at 0 °C and 1.000 atm. A plot of the experimental data of its volume against the Celsius temperature, θ , at constant p , gives a straight line of slope 0.0741 dm³ °C⁻¹. From these data alone (without making use of the perfect gas law), determine the absolute zero of temperature in degrees Celsius.

E1A.25 A vessel of volume 22.4 dm³ contains 1.5 mol H₂(g) and 2.5 mol N₂(g) at 273.15 K. Calculate (i) the mole fractions of each component, (ii) their partial pressures, and (iii) their total pressure.

Problems

P1A.1 A manometer consists of a U-shaped tube containing a liquid. One side is connected to the apparatus and the other is open to the atmosphere. The pressure p inside the apparatus is given by $p = p_a + \rho gh$, where p_a is the external

pressure, ρ is the mass density of the liquid in the tube, $g = 9.806 \text{ m s}^{-2}$ is the acceleration of free fall, and h is the difference in heights of the liquid in the two sides of the tube. (The quantity ρgh is the *hydrostatic pressure* exerted by

FOCUS 4 Physical transformations of pure substances

Integrated activities

I4.1 Construct the phase diagram for benzene near its triple point at 36 Torr and 5.50 °C from the following data: $\Delta_{\text{vap}}H = 10.6 \text{ kJ mol}^{-1}$, $\Delta_{\text{fus}}H = 30.8 \text{ kJ mol}^{-1}$, $\rho(\text{s}) = 0.891 \text{ g cm}^{-3}$, $\rho(\text{l}) = 0.879 \text{ g cm}^{-3}$.

I4.2 In an investigation of thermophysical properties of methylbenzene R.D. Goodwin (*J. Phys. Chem. Ref. Data* 18, 1565 (1989)) presented expressions for two coexistence curves. The solid-liquid curve is given by

$$p/\text{bar} = p_1/\text{bar} + 1000(5.60 + 11.727x)$$

where $x = T/T_1 - 1$ and the triple point pressure and temperature are $p_1 = 0.4362 \text{ pbar}$ and $T_1 = 178.15 \text{ K}$. The liquid-vapour curve is given by

$$\ln(p/\text{bar}) = -10.418/y + 21.157 - 15.996y + 14.015y^2 - 5.0120y^3 + 4.7334(1-y)^{10}$$

(c) Plot $T_{\text{tr}}(\Delta_{\text{sub}}H_{\text{tr}}/\Delta_{\text{sub}}S_{\text{tr}})$ for $5 \leq N \leq 20$. At what value of N does T_{tr} change by less than 1 per cent when N increases by 1?

I4.4 A substance as well-known as methane still receives research attention because it is an important component of natural gas, a commonly used fossil fuel. Friend et al. have published a review of thermophysical properties of methane (D.G. Friend, J.E. Ely, and H. Ingham, *J. Phys. Chem. Ref. Data* 18, 583 (1989)), which included the following vapour pressure data describing the liquid-vapour coexistence curve.

T/K 100 108 110 112 114 120 130 140 150 160 170 190
p/MPa 0.034 0.074 0.088 0.104 0.122 0.192 0.368 0.642 1.041 1.593 2.329 4.521

(a) Plot the liquid-vapour coexistence curve. (b) Estimate the standard boiling point of methane. (c) Compute the standard enthalpy of vaporization of methane (at the standard boiling point), given that the molar volumes of

TAKING YOUR LEARNING FURTHER

'Impact' sections

'Impact' sections show you how physical chemistry is applied in a variety of modern contexts. They showcase physical chemistry as an evolving subject. These sections are listed at the beginning of the text, and are referred to at appropriate places elsewhere. You can find a compilation of 'Impact' sections at the end of the e-book.

A deeper look

These sections take some of the material in the text further. Read them if you want to extend your knowledge and see the

details of some of the more advanced derivations. They are listed at the beginning of the text and are referred to where they are relevant. You can find a compilation of Deeper Looks at the end of the e-book.

Group theory tables

If you need character tables, you can find them at the end of the *Resource section*.

TO THE INSTRUCTOR

We have designed the text to give you maximum flexibility in the selection and sequence of Topics, while the grouping of Topics into Focuses helps to maintain the unity of the subject. Additional resources are:

Figures and tables from the book

Lecturers can find the artwork and tables from the book in ready-to-download format. They may be used for lectures without charge (but not for commercial purposes without specific permission).

Key equations

Supplied in Word format so you can download and edit them.

Solutions to exercises, problems, and integrated activities

For the discussion questions, examples, problems, and integrated activities detailed solutions to the even-numbered questions are available to lecturers online, so they can be set as homework or used as discussion points in class.

Lecturer resources are available only to registered adopters of the textbook. To register, simply visit www.oup.com/he/pchem12e and follow the appropriate links.

ABOUT THE AUTHORS



Photograph by Natasha Ellis-Knight.

Peter Atkins is a fellow of Lincoln College, Oxford, and emeritus professor of physical chemistry in the University of Oxford. He is the author of over seventy books for students and a general audience. His texts are market leaders around the globe. A frequent lecturer throughout the world, he has held visiting professorships in France, Israel, Japan, China, Russia, and New Zealand. He was the founding chairman of the Committee on Chemistry Education of the International Union of Pure and Applied Chemistry and was a member of IUPAC's Physical and Biophysical Chemistry Division.



Julio de Paula is Professor of Chemistry at Lewis & Clark College. A native of Brazil, he received a B.A. degree in chemistry from Rutgers, The State University of New Jersey, and a Ph.D. in biophysical chemistry from Yale University. His research activities encompass the areas of molecular spectroscopy, photochemistry, and nanoscience. He has taught courses in general chemistry, physical chemistry, biochemistry, inorganic chemistry, instrumental analysis, environmental chemistry, and writing. Among his professional honours are a Christian and Mary Lindback Award for Distinguished Teaching, a Henry Dreyfus Teacher-Scholar Award, and a STAR Award from the Research Corporation for Science Advancement.



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James Keeler is Associate Professor of Chemistry, University of Cambridge, and Walters Fellow in Chemistry at Selwyn College. He received his first degree and doctorate from the University of Oxford, specializing in nuclear magnetic resonance spectroscopy. He is presently Head of Department, and before that was Director of Teaching in the department and also Senior Tutor at Selwyn College.

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Jeremy Lee, *University of Durham*
Luize Luse, *Heriot-Watt University*
Zoe Macpherson, *University of Strathclyde*
Sukhbir Mann, *University College London*
Declan Meehan, *Trinity College Dublin*
Eva Pogacar, *Heriot-Watt University*
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CONVENTIONS

To avoid intermediate rounding errors, but to keep track of values in order to be aware of values and to spot numerical errors, we display intermediate results as $n.nnn. . .$ and round the calculation only at the final step.

PHYSICAL CHEMISTRY: PEOPLE AND PERSPECTIVES

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ENERGY A First Look

Much of chemistry is concerned with the transfer and transformation of energy, so right from the outset it is important to become familiar with this concept. The first ideas about energy emerged from **classical mechanics**, the theory of motion formulated by Isaac Newton in the seventeenth century. In the twentieth century classical mechanics gave way to **quantum mechanics**, the theory of motion formulated for the description of small particles, such as electrons, atoms, and molecules. In quantum mechanics the concept of energy not only survived but was greatly enriched, and has come to underlie the whole of physical chemistry.

1 Force

Classical mechanics is formulated in terms of the forces acting on particles, and shows how the paths of particles respond to them by accelerating or changing direction. Much of the discussion focuses on a quantity called the ‘momentum’ of the particle.

(a) Linear momentum

‘Translation’ is the motion of a particle through space. The **velocity**, v , of a particle is the rate of change of its position. Velocity is a ‘vector quantity’, meaning that it has both a direction and a magnitude, and is expressed in terms of how fast the particle travels with respect to x -, y -, and z -axes (Fig. 1).

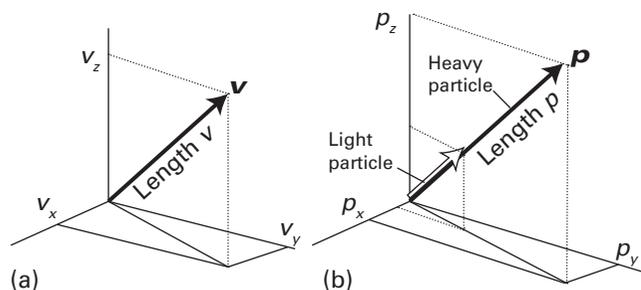


Figure 1 (a) The velocity v is denoted by a vector of magnitude v (the speed) and an orientation that indicates the direction of translational motion. (b) Similarly, the linear momentum p is denoted by a vector of magnitude p and an orientation that corresponds to the direction of motion.

For example, the x -component, v_x , is the particle’s rate of change of position along the x -axis:

$$v_x = \frac{dx}{dt} \quad \text{Component of velocity [definition]} \quad (1a)$$

Similar expressions may be written for the y - and z -components. The magnitude of the velocity, as represented by the length of the velocity vector, is the **speed**, v . Speed is related to the components of velocity by

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2} \quad \text{Speed [definition]} \quad (1b)$$

The **linear momentum**, p , of a particle, like the velocity, is a vector quantity, but takes into account the mass of the particle as well as its speed and direction. Its components are p_x , p_y , and p_z along each axis (Fig. 1b) and its magnitude is p . A heavy particle travelling at a certain speed has a greater linear momentum than a light particle travelling at the same speed. For a particle of mass m , the x -component of the linear momentum is given by

$$p_x = mv_x \quad \text{Component of linear momentum [definition]} \quad (2)$$

and similarly for the y - and z -components.

Brief illustration 1

Imagine a particle of mass m attached to a spring. When the particle is displaced from its equilibrium position and then released, it oscillates back and forth about this equilibrium position. This model can be used to describe many features of a chemical bond. In an idealized case, known as the *simple harmonic oscillator*, the displacement from equilibrium $x(t)$ varies with time as

$$x(t) = A \sin 2\pi \nu t$$

In this expression, ν (nu) is the frequency of the oscillation and A is its amplitude, the maximum value of the displacement along the x -axis. The x -component of the velocity of the particle is therefore

$$v_x = \frac{dx}{dt} = \frac{d(A \sin 2\pi \nu t)}{dt} = 2\pi \nu A \cos 2\pi \nu t$$

The x -component of the linear momentum of the particle is

$$p_x = mv_x = 2\pi \nu A m \cos 2\pi \nu t$$

(b) Angular momentum

'Rotation' is the change of orientation in space around a central point (the 'centre of mass'). Its description is very similar to that of translation but with 'angular velocity' taking the place of velocity and 'moment of inertia' taking the place of mass. The **angular velocity**, ω (omega) is the rate of change of orientation (for example, in radians per second); it is a vector with magnitude ω . The **moment of inertia**, I , is a measure of the mass that is being swung round by the rotational motion. For a particle of mass m moving in a circular path of radius r , the moment of inertia is

$$I = mr^2 \quad \text{Moment of inertia [definition]} \quad (3a)$$

For a molecule composed of several atoms, each atom i gives a contribution of this kind, and the moment of inertia around a given axis is

$$I = \sum_i m_i r_i^2 \quad (3b)$$

where r_i is the perpendicular distance from the mass m_i to the axis. The rotation of a particle is described by its **angular momentum**, J , a vector with a length that indicates the rate at which the particle circulates and a direction that indicates the axis of rotation (Fig. 2). The components of angular momentum, J_x , J_y , and J_z , on three perpendicular axes show how much angular momentum is associated with rotation around each axis. The magnitude J of the angular momentum is

$$J = I\omega \quad \text{Magnitude of angular momentum [definition]} \quad (4)$$

Brief illustration 2

A CO₂ molecule is linear, and the length of each CO bond is 116 pm. The mass of each ¹⁶O atom is $16.00m_u$, where $m_u = 1.661 \times 10^{-27}$ kg. It follows that the moment of inertia of the molecule around an axis perpendicular to the axis of the molecule and passing through the C atom is

$$\begin{aligned} I &= m_o R^2 + 0 + m_o R^2 = 2m_o R^2 \\ &= 2 \times (16.00 \times 1.661 \times 10^{-27} \text{ kg}) \times (1.16 \times 10^{-10} \text{ m})^2 \\ &= 7.15 \times 10^{-46} \text{ kg m}^2 \end{aligned}$$

(c) Newton's second law of motion

The central concept of classical mechanics is **Newton's second law of motion**, which states that *the rate of change of momentum is equal to the force acting on the particle*. This law underlies the calculation of the **trajectory** of a particle, a statement about where it is and where it is moving at each moment of time. Like

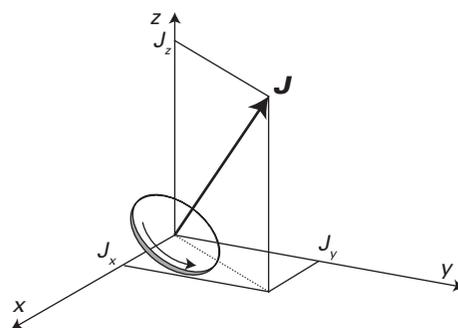


Figure 2 The angular momentum J of a particle is represented by a vector along the axis of rotation and perpendicular to the plane of rotation. The length of the vector denotes the magnitude J of the angular momentum. The direction of motion is clockwise to an observer looking in the direction of the vector.

the velocity and momentum, the **force**, F , is a vector quantity with a direction and a magnitude (the 'strength' of the force). Force is reported in newtons, with $1 \text{ N} = 1 \text{ kg m s}^{-2}$. For motion along the x -axis Newton's second law states that

$$\frac{dp_x}{dt} = F_x \quad \text{Newton's second law [in one dimension]} \quad (5a)$$

where F_x is the component of the force acting along the x -axis. Each component of linear momentum obeys the same kind of equation, so the vector p changes with time as

$$\frac{dp}{dt} = F \quad \text{Newton's second law [vector form]} \quad (5b)$$

Equation 5 is the **equation of motion** of the particle, the equation that has to be solved to calculate its trajectory.

Brief illustration 3

According to 'Hooke's law', the force acting on a particle undergoing harmonic motion (like that in *Brief illustration 2*) is proportional to the displacement and directed opposite to the direction of motion, so in one dimension

$$F_x = -k_f x$$

where x is the displacement from equilibrium and k_f is the 'force constant', a measure of the stiffness of the spring (or chemical bond). It then follows that the equation of motion of a particle undergoing harmonic motion is $dp_x/dt = -k_f x$. Then, because $p_x = mv_x$ and $v_x = dx/dt$, it follows that $dp_x/dt = mdv_x/dt = md^2x/dt^2$. With this substitution, the equation of motion becomes

$$m \frac{d^2x}{dt^2} = -kx$$

Equations of this kind, which are called ‘differential equations’, are solved by special techniques. In most cases in this text, the solutions are simply stated without going into the details of how they are found.

Similar considerations apply to rotation. The change in angular momentum of a particle is expressed in terms of the torque, T , a twisting force. The analogue of eqn 5b is then

$$\frac{dJ}{dt} = T \quad (6)$$

Quantities that describe translation and rotation are analogous, as shown below:

Property	Translation	Rotation
Rate	linear velocity, v	angular velocity, ω
Resistance to change	mass, m	moment of inertia, I
Momentum	linear momentum, p	angular momentum, J
Influence on motion	force, F	torque, T

2 Energy

Energy is a powerful and essential concept in science; nevertheless, its actual nature is obscure and it is difficult to say what it ‘is’. However, it can be related to processes that can be measured and can be defined in terms of the measurable process called work.

(a) Work

Work, w , is done in order to achieve motion against an opposing force. The work needed to be done to move a particle through the infinitesimal distance dx against an opposing force F_x is

$$dw_{\text{on the particle}} = -F_x dx \quad \text{Work [definition]} \quad (7a)$$

When the force is directed to the left (to negative x), F_x is negative, so for motion to the right (dx positive), the work that must be done to move the particle is positive. With force in newtons and distance in metres, the units of work are joules (J), with $1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ s}^{-2}$.

The total work that has to be done to move a particle from x_{initial} to x_{final} is found by integrating eqn 7a, allowing for the possibility that the force may change at each point along the path:

$$w_{\text{on the particle}} = -\int_{x_{\text{initial}}}^{x_{\text{final}}} F_x dx \quad \text{Work} \quad (7b)$$

Brief illustration 4

Suppose that when a bond is stretched from its equilibrium value R_e to some arbitrary value R there is a restoring force proportional to the displacement $x = R - R_e$ from the equilibrium length. Then

$$F_x = -k_f(R - R_e) = -k_f x$$

The constant of proportionality, k_f , is the force constant introduced in *Brief illustration 3*. The total work needed to move an atom so that the bond stretches from zero displacement ($x_{\text{initial}} = 0$), when the bond has its equilibrium length, to a displacement $x_{\text{final}} = R_{\text{final}} - R_e$ is

$$\begin{aligned} w_{\text{on an atom}} &= -\int_0^{x_{\text{final}}} (-k_f x) dx = k_f \int_0^{x_{\text{final}}} x dx \\ &= \frac{1}{2} k_f x_{\text{final}}^2 = \frac{1}{2} k_f (R_{\text{final}} - R_e)^2 \end{aligned} \quad \text{Integral A.1}$$

(All the integrals required in this book are listed in the *Resource section*.) The work required increases as the square of the displacement: it takes four times as much work to stretch a bond through 20 pm as it does to stretch the same bond through 10 pm.

(b) The definition of energy

Now we get to the core of this discussion. **Energy is the capacity to do work.** An object with a lot of energy can do a lot of work; one with little energy can do only little work. Thus, a spring that is compressed can do a lot of work as it expands, so it is said to have a lot of energy. Once the spring is expanded it can do only a little work, perhaps none, so it is said to have only a little energy. The SI unit of energy is the same as that of work, namely the joule, with $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$.

A particle may possess two kinds of energy, kinetic energy and potential energy. The **kinetic energy**, E_k , of a particle is the energy it possesses as a result of its motion. For a particle of mass m travelling at a speed v ,

$$E_k = \frac{1}{2} m v^2 \quad \text{Kinetic energy [definition]} \quad (8a)$$

A particle with a lot of kinetic energy can do a lot of work, in the sense that if it collides with another particle it can cause it to move against an opposing force. Because the magnitude of the linear momentum and speed are related by $p = mv$, so $v = p/m$, an alternative version of this relation is

$$E_k = \frac{p^2}{2m} \quad (8b)$$

It follows from Newton’s second law that if a particle is initially stationary and is subjected to a constant force then its linear momentum increases from zero. Because the magnitude of the

applied force may be varied at will, the momentum and therefore the kinetic energy of the particle may be increased to any value.

The **potential energy**, E_p or V , of a particle is the energy it possesses as a result of its position. For instance, a stationary weight high above the surface of the Earth can do a lot of work as it falls to a lower level, so is said to have more energy, in this case potential energy, than when it is resting on the surface of the Earth.

This definition can be turned around. Suppose the weight is returned from the surface of the Earth to its original height. The work needed to raise it is equal to the potential energy that it once again possesses. For an infinitesimal change in height, dx , that work is $-F_x dx$. Therefore, the infinitesimal change in potential energy is $dE_p = -F_x dx$. This equation can be rearranged into a relation between the force and the potential energy:

$$F_x = -\frac{dE_p}{dx} \quad \text{or} \quad F_x = -\frac{dV}{dx} \quad \text{Relation of force to potential energy} \quad (9)$$

No *universal* expression for the dependence of the potential energy on position can be given because it depends on the type of force the particle experiences. However, there are two very important specific cases where an expression can be given. For a particle of mass m at an altitude h close to the surface of the Earth, the **gravitational potential energy** is

$$E_p(h) = E_p(0) + mgh \quad \text{Gravitational potential energy [close to surface of the Earth]} \quad (10)$$

where g is the **acceleration of free fall** (g depends on location, but its 'standard value' is close to 9.81 m s^{-2}). The zero of potential energy is arbitrary. For a particle close to the surface of the Earth, it is common to set $E_p(0) = 0$.

The other very important case (which occurs whenever the structures of atoms and molecules are discussed), is the electrostatic potential energy between two electric charges Q_1 and Q_2 at a separation r in a vacuum. This **Coulomb potential energy** is

$$E_p(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \quad \text{Coulomb potential energy [in a vacuum]} \quad (11)$$

Charge is expressed in coulombs (C). The constant ϵ_0 (epsilon zero) is the **electric constant** (or *vacuum permittivity*), a fundamental constant with the value $8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$. It is conventional (as in eqn 11) to set the potential energy equal to zero at infinite separation of charges.

The **total energy** of a particle is the sum of its kinetic and potential energies:

$$E = E_k + E_p, \quad \text{or} \quad E = E_k + V \quad \text{Total energy} \quad (12)$$

A fundamental feature of nature is that *energy is conserved*; that is, energy can neither be created nor destroyed. Although

energy can be transformed from one form to another, its total is constant.

An alternative way of thinking about the potential energy arising from the interaction of charges is in terms of the **potential**, which is a measure of the 'potential' of one charge to affect the potential energy of another charge when the second charge is brought into its vicinity. A charge Q_1 gives rise to a **Coulomb potential** ϕ_1 (phi) such that the potential energy of the interaction with a second charge Q_2 is $Q_2\phi_1(r)$. Comparison of this expression with eqn 11 shows that

$$\phi_1(r) = \frac{Q_1}{4\pi\epsilon_0 r} \quad \text{Coulomb potential [in a vacuum]} \quad (13)$$

The units of potential are joules per coulomb, J C^{-1} , so when the potential is multiplied by a charge in coulombs, the result is the potential energy in joules. The combination joules per coulomb occurs widely and is called a volt (V): $1 \text{ V} = 1 \text{ J C}^{-1}$.

The language developed here inspires an important alternative energy unit, the **electronvolt** (eV): 1 eV is defined as the potential energy acquired when an electron is moved through a potential difference of 1 V. The relation between electronvolts and joules is

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

Many processes in chemistry involve energies of a few electronvolts. For example, to remove an electron from a sodium atom requires about 5 eV.

3 Temperature

A key idea of quantum mechanics is that the translational energy of a molecule, atom, or electron that is confined to a region of space, and any rotational or vibrational energy that a molecule possesses, is **quantized**, meaning that it is restricted to certain discrete values. These permitted energies are called **energy levels**. The values of the permitted energies depend on the characteristics of the particle (for instance, its mass) and for translation the extent of the region to which it is confined. The allowed energies are widest apart for particles of small mass confined to small regions of space. Consequently, quantization must be taken into account for electrons bound to nuclei in atoms and molecules. It can be ignored for macroscopic bodies, for which the separation of all kinds of energy levels is so small that for all practical purposes their energy can be varied virtually continuously.

Figure 3 depicts the typical energy level separations associated with rotational, vibrational, and electronic motion. The separation of rotational energy levels (in small molecules, about 10^{-21} J , corresponding to about 0.6 kJ mol^{-1}) is smaller than that of vibrational energy levels (about 10^{-20} – 10^{-19} J , or

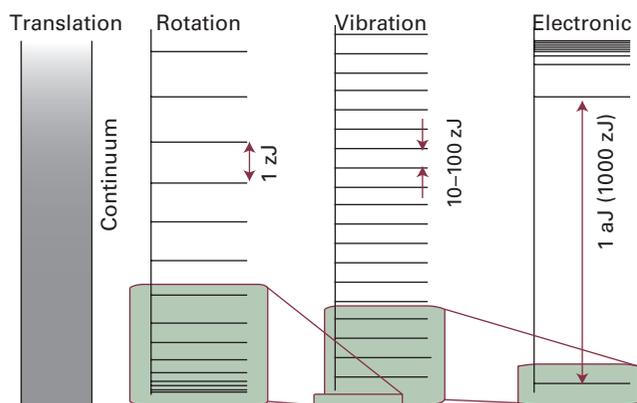


Figure 3 The energy level separations typical of four types of system. (1 zJ = 10^{-21} J; in molar terms, 1 zJ is equivalent to about 0.6 kJ mol^{-1} .)

$6\text{--}60 \text{ kJ mol}^{-1}$), which itself is smaller than that of electronic energy levels (about 10^{-18} J, corresponding to about 600 kJ mol^{-1}).

(a) The Boltzmann distribution

The continuous thermal agitation that molecules experience in a sample ensures that they are distributed over the available energy levels. This distribution is best expressed in terms of the occupation of states. The distinction between a state and a level is that a given level may be comprised of several states all of which have the same energy. For instance, a molecule might be rotating clockwise with a certain energy, or rotating counter-clockwise with the same energy. One particular molecule may be in a state belonging to a low energy level at one instant, and then be excited into a state belonging to a high energy level a moment later. Although it is not possible to keep track of which state each molecule is in, it is possible to talk about the *average* number of molecules in each state. A remarkable feature of nature is that, for a given array of energy levels, how the molecules are distributed over the states depends on a single parameter, the ‘temperature’, T .

The **population** of a state is the average number of molecules that occupy it. The populations, whatever the nature of the states (translational, rotational, and so on), are given by a formula derived by Ludwig Boltzmann and known as the **Boltzmann distribution**. According to Boltzmann, the ratio of the populations of states with energies ϵ_i and ϵ_j is

$$\frac{N_i}{N_j} = e^{-(\epsilon_i - \epsilon_j)/kT} \quad \text{Boltzmann distribution} \quad (14a)$$

where k is **Boltzmann’s constant**, a fundamental constant with the value $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$ and T is the **temperature**, the parameter that specifies the relative populations of states, regardless of their type. Thus, when $T = 0$, the populations of all states other than the lowest state (the ‘ground state’) of the

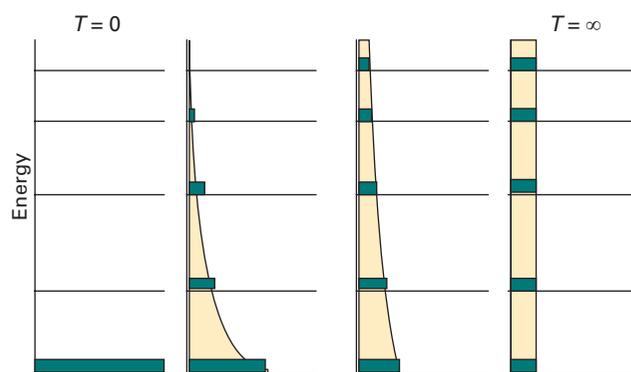


Figure 4 The Boltzmann distribution of populations (represented by the horizontal bars) for a system of five states with different energies as the temperature is raised from zero to infinity. *Interact with the dynamic version of this graph in the e-book.*

molecule are zero. As the value of T is increased (the ‘temperature is raised’), the populations of higher energy states increase, and the distribution becomes more uniform. This behaviour is illustrated in Fig. 4 for a system with five states of different energy. As predicted by eqn 14a, as the temperature approaches infinity ($T \rightarrow \infty$), the states become equally populated.

In chemical applications it is common to use molar energies, $E_{m,i}$, with $E_{m,i} = N_A \epsilon_i$, where N_A is Avogadro’s constant. Then eqn 14a becomes

$$\frac{N_i}{N_j} = e^{-(E_{m,i}/N_A - E_{m,j}/N_A)/kT} = e^{-(E_{m,i} - E_{m,j})/N_A kT} = e^{-(E_{m,i} - E_{m,j})/RT} \quad (14b)$$

where $R = N_A k$. The constant R is known as the ‘gas constant’; it appears in expressions of this kind when molar, rather than molecular, energies are specified. Moreover, because it is simply the molar version of the more fundamental Boltzmann constant, it occurs in contexts other than gases.

Brief illustration 5

Methylcyclohexane molecules may exist in one of two conformations, with the methyl group in either an equatorial or axial position. The equatorial form lies 6.0 kJ mol^{-1} lower in energy than the axial form. The relative populations of molecules in the axial and equatorial states at 300 K are therefore

$$\begin{aligned} \frac{N_{\text{axial}}}{N_{\text{equatorial}}} &= e^{-(E_{m,\text{axial}} - E_{m,\text{equatorial}})/RT} \\ &= e^{-(6.0 \times 10^3 \text{ J mol}^{-1}) / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \\ &= 0.090 \end{aligned}$$

The number of molecules in an axial conformation is therefore just 9 per cent of those in the equatorial conformation.

The important features of the Boltzmann distribution to bear in mind are:

- The distribution of populations is an exponential function of energy and the temperature. As the temperature is increased, states with higher energy become progressively more populated.
- States closely spaced in energy compared to kT are more populated than states that are widely spaced compared to kT .

The energy spacings of translational and rotational states are typically much less than kT at room temperature. As a result, many translational and rotational states are populated. In contrast, electronic states are typically separated by much more than kT . As a result, only the ground electronic state of a molecule is occupied at normal temperatures. Vibrational states are widely separated in small, stiff molecules and only the ground vibrational state is populated. Large and flexible molecules are also found principally in their ground vibrational state, but might have a few higher energy vibrational states populated at normal temperatures.

(b) The equipartition theorem

For gases consisting of non-interacting particles it is often possible to calculate the average energy associated with each type

of motion by using the **equipartition theorem**. This theorem arises from a consideration of how the energy levels associated with different kinds of motion are populated according to the Boltzmann distribution. The theorem states that

At thermal equilibrium, the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$.

A 'quadratic contribution' is one that is proportional to the square of the momentum or the square of the displacement from an equilibrium position. For example, the kinetic energy of a particle travelling in the x -direction is $E_k = p_x^2/2m$. This motion therefore makes a contribution of $\frac{1}{2}kT$ to the energy.

The energy of vibration of atoms in a chemical bond has *two* quadratic contributions. One is the kinetic energy arising from the back and forth motion of the atoms. Another is the potential energy which, for the harmonic oscillator, is $E_p = \frac{1}{2}k_f x^2$ and is a second quadratic contribution. Therefore, the total average energy is $\frac{1}{2}kT + \frac{1}{2}kT = kT$.

The equipartition theorem applies only if many of the states associated with a type of motion are populated. At temperatures of interest to chemists this condition is always met for translational motion, and is usually met for rotational motion. Typically, the separation between vibrational and electronic states is greater than for rotation or translation, and as only a few states are occupied (often only one, the ground state), the equipartition theorem is unreliable for these types of motion.

Checklist of concepts

- | | |
|--|---|
| <ul style="list-style-type: none"> <input type="checkbox"/> 1. Newton's second law of motion states that the rate of change of momentum is equal to the force acting on the particle. <input type="checkbox"/> 2. Work is done in order to achieve motion against an opposing force. Energy is the capacity to do work. <input type="checkbox"/> 3. The kinetic energy of a particle is the energy it possesses as a result of its motion. <input type="checkbox"/> 4. The potential energy of a particle is the energy it possesses as a result of its position. <input type="checkbox"/> 5. The total energy of a particle is the sum of its kinetic and potential energies. | <ul style="list-style-type: none"> <input type="checkbox"/> 6. The Coulomb potential energy between two charges separated by a distance r varies as $1/r$. <input type="checkbox"/> 7. The energy levels of confined particles are quantized, as are those of rotating or vibrating molecules. <input type="checkbox"/> 8. The Boltzmann distribution is a formula for calculating the relative populations of states of various energies. <input type="checkbox"/> 9. The equipartition theorem states that for a sample at thermal equilibrium the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$. |
|--|---|

Checklist of equations

Property	Equation	Comment	Equation number
Component of velocity in x direction	$v_x = dx/dt$	Definition; likewise for y and z	1a
Component of linear momentum in x direction	$p_x = mv_x$	Definition; likewise for y and z	2
Moment of inertia	$I = mr^2$	Point particle	3a
	$I = \sum_i m_i r_i^2$	Molecule	3b
Angular momentum	$J = I\omega$		4
Equation of motion	$F_x = dp_x/dt$	Motion along x -direction	5a
	$F = dp/dt$	Newton's second law of motion	5b
	$T = dJ/dt$	Rotational motion	6
Work opposing a force in the x direction	$dw = -F_x dx$	Definition	7a
Kinetic energy	$E_k = \frac{1}{2}mv^2$	Definition; v is the speed	8a
Potential energy and force	$F_x = -dV/dx$	One dimension	9
Coulomb potential energy	$E_p(r) = Q_1 Q_2 / 4\pi\epsilon_0 r$	In a vacuum	11
Coulomb potential	$\phi_1(r) = Q_1 / 4\pi\epsilon_0 r$	In a vacuum	13
Boltzmann distribution	$N_i/N_j = e^{-(\epsilon_i - \epsilon_j)/kT}$		14a

Atkins'

PHYSICAL CHEMISTRY

FOCUS 1

The properties of gases

A gas is a form of matter that fills whatever container it occupies. This Focus establishes the properties of gases that are used throughout the text.

1A The perfect gas

This Topic is an account of an idealized version of a gas, a ‘perfect gas’, and shows how its equation of state may be assembled from the experimental observations summarized by Boyle’s law, Charles’s law, and Avogadro’s principle.

1A.1 Variables of state; 1A.2 Equations of state

1B The kinetic model

A central feature of physical chemistry is its role in building models of molecular behaviour that seek to explain observed phenomena. A prime example of this procedure is the development of a molecular model of a perfect gas in terms of a collection of molecules (or atoms) in ceaseless, essentially random motion. As well as accounting for the gas laws, this model can be used to predict the average speed at which molecules move in a gas, and its dependence on temperature. In combination with the Boltzmann distribution (see *Energy: A first look*), the model can also be used to predict the spread of molecular speeds and its dependence on molecular mass and temperature.

1B.1 The model; 1B.2 Collisions

1C Real gases

The perfect gas is a starting point for the discussion of properties of all gases, and its properties are invoked throughout thermodynamics. However, actual gases, ‘real gases’, have properties that differ from those of perfect gases, and it is necessary to be able to interpret these deviations and build the effects of molecular attractions and repulsions into the model. The discussion of real gases is another example of how initially primitive models in physical chemistry are elaborated to take into account more detailed observations.

1C.1 Deviations from perfect behaviour; 1C.2 The van der Waals equation

What is an application of this material?

The perfect gas law and the kinetic theory can be applied to the study of phenomena confined to a reaction vessel or encompassing an entire planet or star. In *Impact 1*, accessed via the e-book, the gas laws are used in the discussion of meteorological phenomena—the weather. *Impact 2*, accessed via the e-book, examines how the kinetic model of gases has a surprising application: to the discussion of dense stellar media, such as the interior of the Sun.

► Go to the e-book for videos that feature the derivation and interpretation of equations, and applications of this material.

TOPIC 1A The perfect gas

► Why do you need to know this material?

The relation between the pressure, volume, and temperature of a perfect gas is used extensively in the development of quantitative theories about the physical and chemical behaviour of real gases. It is also used extensively throughout thermodynamics.

► What is the key idea?

The perfect gas law, which describes the relation between the pressure, volume, temperature, and amount of substance, is a limiting law that is obeyed increasingly well as the pressure of a gas tends to zero.

► What do you need to know already?

You need to know how to handle quantities and units in calculations, as reviewed in the *Resource section*.

The properties of gases were among the first to be established quantitatively (largely during the seventeenth and eighteenth centuries) when the technological requirements of travel in balloons stimulated their investigation. This Topic reviews how the physical state of a gas is described using variables such as pressure and temperature, and then discusses how these variables are related.

1A.1 Variables of state

The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties. Two samples of the same substance that have the same physical properties are said to be ‘in the same state’. The **variables of state**, the variables needed to specify the state of a system, are the amount of substance it contains, n ; the volume it occupies, V ; the pressure, p ; and the temperature, T .

1A.1(a) Pressure and volume

The **pressure**, p , that an object experiences is defined as the force, F , applied divided by the area, A , to which that force is applied. A gas exerts a pressure on the walls of its container as a result of the collisions between the molecules and the walls:

these collisions are so numerous that the force, and hence the pressure, is steady.

The SI unit of pressure is the *pascal*, Pa, defined as $1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$. Several other units are still widely used, and the relations between them are given in Table 1A.1. Because many physical properties depend on the pressure acting on a sample, it is appropriate to select a certain value of the pressure to report their values. The **standard pressure**, p^\ominus , for reporting physical quantities is currently defined as $p^\ominus = 1 \text{ bar}$ (that is, 10^5 Pa) exactly. This pressure is close to, but not the same as, 1 atm, which is typical for everyday conditions.

Consider the arrangement shown in Fig. 1A.1 where two gases in separate containers share a common movable wall. In Fig. 1A.1a the gas on the left is at higher pressure than that on the right, and so the force exerted on the wall by the gas on the left is greater than that exerted by the gas on the right. As a result, the wall moves to the right, the pressure on the left

Table 1A.1 Pressure units*

Name	Symbol	Value
pascal	Pa	1 Pa = 1 N m⁻², 1 kg m⁻¹ s⁻²
bar	bar	1 bar = 10⁵ Pa
atmosphere	atm	1 atm = 101.325 kPa
torr	Torr	1 Torr = (101 325/760) Pa = 133.32 ... Pa
millimetres of mercury	mmHg	1 mmHg = 133.322 ... Pa
pounds per square inch	psi	1 psi = 6.894757 ... kPa

* Values in bold are exact.

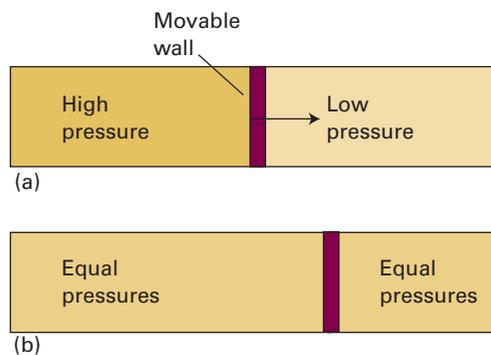


Figure 1A.1 (a) When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into the low pressure region until the pressures are equal. (b) When the two pressures are identical, the wall will stop moving. At this point there is mechanical equilibrium between the two regions.

decreases, and that on the right increases. Eventually (as in Fig. 1A.1b) the two pressures become equal and the wall no longer moves. This condition of equality of pressure on either side of a movable wall is a state of **mechanical equilibrium** between the two gases.

The pressure exerted by the atmosphere is measured with a *barometer*. The original version of a barometer (which was invented by Torricelli, a student of Galileo) involved taking a glass tube, sealed at one end, filling it with mercury and then up-ending it (without letting in any air) into a bath of mercury. The pressure of the atmosphere acting on the surface of the mercury in the bath supports a column of mercury of a certain height in the tube: the pressure at the base of the column, due to the mercury in the tube, is equal to the atmospheric pressure. As the atmospheric pressure changes, so does the height of the column.

The pressure of gas in a container, and also now the atmosphere, is measured by using a pressure gauge, which is a device with properties that respond to pressure. For instance, in a *Bayard–Alpert pressure gauge* the molecules present in the gas are ionized and the resulting current of ions is interpreted in terms of the pressure. In a *capacitance manometer*, two electrodes form a capacitor. One electrode is fixed and the other is a diaphragm which deflects as the pressure changes. This deflection causes a change in the capacitance, which is measured and interpreted as a pressure. Certain semiconductors also respond to pressure and are used as transducers in solid-state pressure gauges, including those in mobile phones (cell phones).

The **volume**, V , of a gas is a measure of the extent of the region of space it occupies. The SI unit of volume is m^3 .

1A.1(b) Temperature

The temperature is formally a property that determines in which direction energy will flow as heat when two samples are placed in contact through thermally conducting walls: energy flows from the sample with the higher temperature to the sample with the lower temperature. The symbol T denotes the **thermodynamic temperature**, which is an absolute scale with $T=0$ as the lowest point. Temperatures above $T=0$ are expressed by using the **Kelvin scale**, in which the gradations of temperature are expressed in *kelvins* (K; not $^\circ\text{K}$). Until 2019, the Kelvin scale was defined by setting the triple point of water (the temperature at which ice, liquid water, and water vapour are in mutual equilibrium) at exactly 273.16 K. The scale has now been redefined by referring it to the more precisely known value of the Boltzmann constant.

There are many devices used to measure temperature. They vary from simple devices that measure the expansion of a liquid along a tube, as commonly found in laboratories, to electronic devices where the resistance of a material or the potential difference developed at a junction is related to the temperature.

The **Celsius scale** of temperature is commonly used to express temperatures. In this text, temperatures on the Celsius scale are denoted θ (theta) and expressed in *degrees Celsius* ($^\circ\text{C}$). The thermodynamic and Celsius temperatures are related by the exact expression

$$T/\text{K} = \theta/^\circ\text{C} + 273.15 \quad \text{Celsius scale [definition]} \quad (1A.1)$$

This relation is the definition of the Celsius scale in terms of the more fundamental Kelvin scale. It implies that a difference in temperature of 1°C is equivalent to a difference of 1 K.

The lowest temperature on the thermodynamic temperature scale is written $T=0$, not $T=0\text{ K}$. This scale is absolute, and the lowest temperature is 0 regardless of the size of the divisions on the scale (just as zero pressure is denoted $p=0$, regardless of the size of the units, such as bar or pascal). However, it is appropriate to write 0°C because the Celsius scale is not absolute.

1A.1(c) Amount

In day-to-day conversation ‘amount’ has many meanings but in physical science it has a very precise definition. The **amount of substance**, n , is a measure of the number of specified entities present in the sample; these entities may be atoms, or molecules, or formula units. The SI unit of amount of substance is the mole (mol). The amount of substance is commonly referred to as the ‘chemical amount’ or simply ‘amount’.

Until 2019 the mole was defined as the number of carbon atoms in exactly 12 g of carbon-12. However, it has been redefined such that 1 mol of a substance contains exactly $6.02214076 \times 10^{23}$ entities. The number of entities per mole is called **Avogadro’s constant**, N_A . It follows from the definition of the mole that $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$. Note that N_A is a constant with units, not a pure number. Also, it is not correct to specify amount as the ‘number of moles’: the correct phrase is ‘amount in moles’.

The amount of substance is related to the mass, m , of the substance through the **molar mass**, M , which is the mass per mole of its atoms, its molecules, or its formula units. The SI unit of molar mass is kg mol^{-1} but it is more common to use g mol^{-1} . The amount of substance of specified entities in a sample can readily be calculated from its mass by using

$$n = \frac{m}{M} \quad \text{Amount of substance} \quad (1A.2)$$

1A.1(d) Intensive and extensive properties

Suppose a sample is divided into smaller samples. If a property of the original sample has a value that is equal to the sum of its values in all the smaller samples, then it is said to be an **extensive** property. Amount, mass, and volume are examples of extensive properties. If a property retains the same value as in

the original sample for all the smaller samples, then it is said to be **intensive**. Temperature and pressure are examples of intensive properties.

The value of a property X divided by the amount n gives the **molar value** of that property X_m : that is, $X_m = X/n$. All molar properties are intensive, whereas X and n are both extensive. The mass density, $\rho = m/V$, is also intensive.

Example 1A.1 Specifying the variables of state

When released into a certain vessel, 0.560 mg of nitrogen gas is observed to exert a pressure of 10.4 Torr at a temperature of 25.2 °C. Express the pressure in pascals (Pa) and the thermodynamic temperature in kelvins (K). Also calculate the amount of N_2 , and the number of N_2 molecules present. Take the molar mass of N_2 as 28.02 g mol⁻¹.

Collect your thoughts The SI unit of pressure is Pa, and the conversion from Torr to Pa is given in Table 1A.1; the conversion of °C to K is given by eqn 1A.1. The amount is computed using eqn 1A.2.

The solution From the table 1 Torr = 133.32... Pa, so a pressure of 10.4 Torr is converted to Pa through

$$p = (10.4 \text{ Torr}) \times (133.32 \dots \text{ Pa Torr}^{-1}) = 1.39 \times 10^3 \text{ Pa}$$

Note the inclusion of units for each quantity, and the way in which the units cancel to give the required result. The temperature in °C is converted to K using eqn 1A.1.

$$T/\text{K} = \theta/^\circ\text{C} + 273.15 = (25.2 \text{ }^\circ\text{C})/^\circ\text{C} + 273.15 = 298$$

Thus $T = 298 \text{ K}$. The amount is calculated by using eqn 1A.2: note the conversion of the mass from mg to g so as to match the units of the molar mass.

$$n = \frac{m}{M} = \frac{0.560 \times 10^{-3} \text{ g}}{28.02 \text{ g mol}^{-1}} = 3.99 \dots \times 10^{-5} \text{ mol} = 4.00 \times 10^{-5} \text{ mol}$$

Here the intermediate result is truncated at (not rounded to) three figures, but the final result is rounded to three figures.

The number of molecules is found by multiplying the amount by Avogadro's constant.

$$N = nN_A = (3.99 \dots \times 10^{-5} \text{ mol}) \times (6.0221 \times 10^{23} \text{ mol}^{-1}) = 2.41 \times 10^{19}$$

The result, being a pure number, is dimensionless.

Self-test 1A.1 Express the pressure in bar and in atm.

$$\text{Answer: } 1.39 \times 10^2 \text{ bar or } 1.37 \times 10^{-2} \text{ atm}$$

Exercises

E1A.1 Express (i) 108 kPa in torr and (ii) 0.975 bar in atmospheres.

E1A.2 What mass of methanol (molar mass 32.04 g mol⁻¹) contains the same number of molecules as 1.00 g of ethanol (molar mass 46.07 g mol⁻¹)?

1A.2 Equations of state

Although in principle the state of a pure substance is specified by giving the values of n , V , p , and T , it has been established experimentally that it is sufficient to specify only three of these variables because doing so fixes the value of the fourth variable. That is, it is an experimental fact that each substance is described by an **equation of state**, an equation that interrelates these four variables.

The general form of an equation of state is

$$p = f(T, V, n) \quad \text{General form of an equation of state} \quad (1A.3)$$

This equation means that if the values of n , T , and V are known for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but the explicit form of the equation is known in only a few special cases. One very important example is the equation of state of a 'perfect gas', which has the form $p = nRT/V$, where R is a constant independent of the identity of the gas.

1A.2(a) The empirical basis of the perfect gas law

The equation of state of a perfect gas was established by combining a series of empirical laws that arose from experimental observations. These laws can be summarized as

Boyle's law: $pV = \text{constant}$, at constant n, T

Charles's law: $V = \text{constant} \times T$, at constant n, p

$p = \text{constant} \times T$, at constant n, V

Avogadro's principle: $V = \text{constant} \times n$, at constant p, T

Boyle's and Charles's laws are strictly true only in the limit that the pressure goes to zero ($p \rightarrow 0$): they are examples of a **limiting law**, a law that is strictly true only in a certain limit. However, these laws are found to be reasonably reliable at normal pressures ($p \approx 1 \text{ bar}$) and are used throughout chemistry. Avogadro's principle is so-called because it supposes that the system consists of molecules whereas a law is strictly a summary of observations and independent of any assumed model.

Figure 1A.2 depicts the variation of the pressure of a sample of gas as the volume is changed. Each of the curves in the graph corresponds to a single temperature and hence is called an **isotherm**. According to Boyle's law, the isotherms of gases are hyperbolas (curves obtained by plotting y against x with $xy = \text{constant}$, or $y = \text{constant}/x$). An alternative depiction, a plot of pressure against $1/\text{volume}$, is shown in Fig. 1A.3; in such a plot the isotherms are straight lines because p is proportional to $1/V$. Note that all the lines extrapolate to the point $p = 0$, $1/V = 0$ but have slopes that depend on the temperature.

The linear variation of volume with temperature summarized by Charles's law is illustrated in Fig. 1A.4. The lines in this

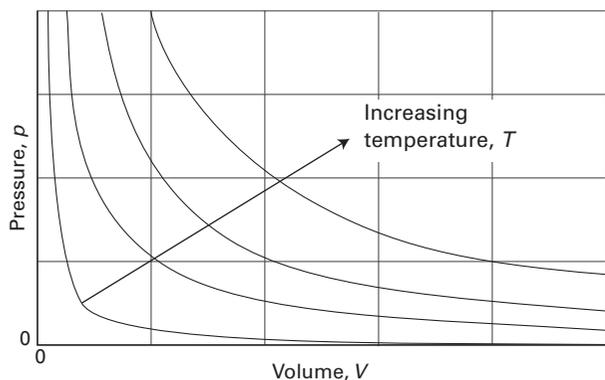


Figure 1A.2 The pressure-volume dependence of a fixed amount of gas that obeys Boyle's law. Each curve is for a different temperature and is called an isotherm; each isotherm is a hyperbola ($pV = \text{constant}$).

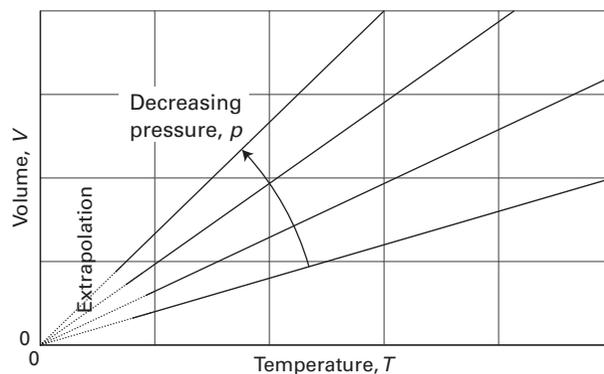


Figure 1A.4 The volume-temperature dependence of a fixed amount of gas that obeys Charles's law. Each line is for a different pressure and is called an isobar. Each isobar is a straight line and extrapolates to zero volume at $T = 0$, corresponding to $\theta = -273.15^\circ\text{C}$.

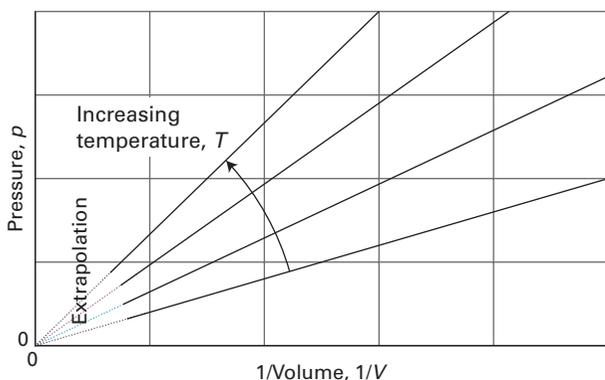


Figure 1A.3 Straight lines are obtained when the pressure of a gas obeying Boyle's law is plotted against $1/V$ at constant temperature. These lines extrapolate to zero pressure at $1/V = 0$.

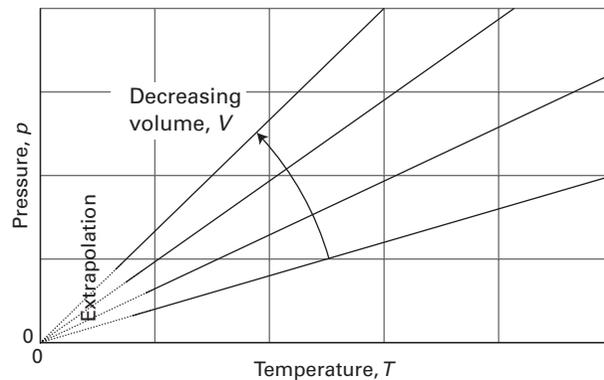


Figure 1A.5 The pressure-temperature dependence of a fixed amount of gas that obeys Charles's law. Each line is for a different volume and is called an isochore. Each isochore is a straight line and extrapolates to zero pressure at $T = 0$.

illustration are examples of **isobars**, or lines showing the variation of properties at constant pressure. All these isobars extrapolate to the point $V = 0$, $T = 0$ and have slopes that depend on the pressure. Figure 1A.5 illustrates the linear variation of pressure with temperature. The lines in this diagram are **isochores**, or lines showing the variation of properties at constant volume, and they all extrapolate to $p = 0$, $T = 0$.

The empirical observations summarized by Boyle's and Charles's laws and Avogadro's principle can be combined into a single expression:

$$pV = \text{constant} \times nT$$

This expression is consistent with Boyle's law, $pV = \text{constant}$ when n and T are constant. It is also consistent with both forms of Charles's law: $p \propto T$ when n and V are held constant, and $V \propto T$ when n and p are held constant. The expression also agrees with Avogadro's principle, $V \propto n$ when p and T are constant. The constant of proportionality, which is found

experimentally to be the same for all gases, is denoted R and called the (molar) **gas constant**. The resulting expression

$$pV = nRT \quad \text{Perfect gas law} \quad (1A.4)$$

is the **perfect gas law** (or *perfect gas equation of state*). A gas that obeys this law exactly under all conditions is called a **perfect gas** (or *ideal gas*). Although the term 'ideal gas' is used widely, in this text we prefer to use 'perfect gas' because there is an important and useful distinction between ideal and perfect. The distinction is that in an 'ideal system' all the interactions between molecules are the same; in a 'perfect system', not only are they the same but they are also zero.

For a **real gas**, any actual gas, the perfect gas law is approximate, but the approximation becomes better as the pressure of the gas approaches zero. In the limit that the pressure goes to zero, $p \rightarrow 0$, the equation is exact. The value of the gas constant R can be determined by evaluating $R = pV/nT$ for a gas in the limit of zero pressure (to guarantee that it is behaving

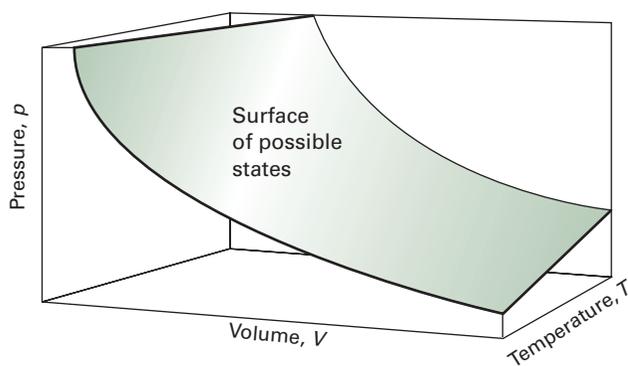


Figure 1A.6 A region of the p, V, T surface of a fixed amount of perfect gas molecules. The points forming the surface represent the only states of the gas that can exist.

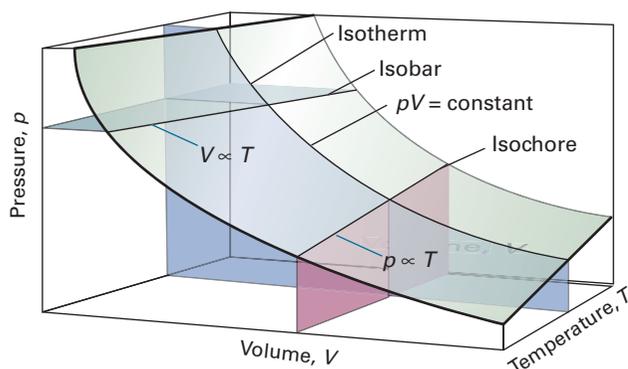


Figure 1A.7 Sections through the surface shown in Fig. 1A.6 at constant temperature give the isotherms shown in Fig. 1A.2. Sections at constant pressure give the isobars shown in Fig. 1A.4. Sections at constant volume give the isochores shown in Fig. 1A.5.

perfectly). As remarked in *Energy: A first look*, the modern procedure is to note that $R = N_A k$, where k is Boltzmann's constant and N_A has its newly defined value, as indicated earlier.

The surface in Fig. 1A.6 is a plot of the pressure of a fixed amount of perfect gas molecules against its volume and thermodynamic temperature as given by eqn 1A.4. The surface depicts the only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface. Figure 1A.7 shows how the graphs in Figs. 1A.2, 1A.4, and 1A.5 correspond to sections through the surface.

Example 1A.2 Using the perfect gas law

Nitrogen gas is introduced into a vessel of constant volume at a pressure of 100 atm and a temperature of 300 K. The temperature is then raised to 500 K. What pressure would the gas then exert, assuming that it behaved as a perfect gas?

Collect your thoughts The pressure is expected to be greater on account of the increase in temperature. The perfect gas law in the form $pV/nT = R$ implies that if the conditions are changed

from one set of values to another, then because pV/nT is equal to a constant, the two sets of values are related by the 'combined gas law'

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \quad \text{Combined gas law} \quad (1A.5)$$

In this case the volume is the same before and after heating, so $V_1 = V_2$ and these terms cancel. Likewise the amount does not change upon heating, so $n_1 = n_2$ and these terms also cancel.

The solution Cancellation of the volumes and amounts on each side of the combined gas law results in

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

which can be rearranged into

$$p_2 = \frac{T_2}{T_1} \times p_1$$

Substitution of the data then gives

$$p_2 = \frac{500 \text{ K}}{300 \text{ K}} \times (100 \text{ atm}) = 167 \text{ atm}$$

Self-test 1A.2 What temperature would be needed for the same sample to exert a pressure of 300 atm?

Answer: 900 K

The molecular explanation of Boyle's law is that if a sample of gas is compressed to half its volume, then twice as many molecules strike the walls in a given period of time than before it was compressed. As a result, the average force exerted on the walls is doubled. Hence, when the volume is halved the pressure of the gas is doubled, and pV is a constant. Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently.

The molecular explanation of Charles's law lies in the fact that raising the temperature of a gas increases the average speed of its molecules. The molecules collide with the walls more frequently and with greater impact. Therefore they exert a greater pressure on the walls of the container. For a quantitative account of these relations, see Topic 1B.

1A.2(b) The value of the gas constant

If the pressure, volume, amount, and temperature are expressed in their SI units the gas constant R has units $\text{N m K}^{-1} \text{mol}^{-1}$ which, because $1 \text{ J} = 1 \text{ N m}$, can be expressed in terms of $\text{J K}^{-1} \text{mol}^{-1}$. The currently accepted value of R is $8.3145 \text{ J K}^{-1} \text{mol}^{-1}$. Other combinations of units for pressure and volume result in different values and units for the gas constant. Some commonly encountered combinations are given in Table 1A.2.

The perfect gas law is of the greatest importance in physical chemistry because it is used to derive a wide range of relations

Table 1A.2 The (molar) gas constant*

R	
8.31447	J K ⁻¹ mol ⁻¹
8.20574 × 10 ⁻²	dm ³ atm K ⁻¹ mol ⁻¹
8.31447 × 10 ⁻²	dm ³ bar K ⁻¹ mol ⁻¹
8.31447	Pa m ³ K ⁻¹ mol ⁻¹
62.364	dm ³ Torr K ⁻¹ mol ⁻¹
1.987 21	cal K ⁻¹ mol ⁻¹

* The gas constant is now defined as $R = N_A k$, where N_A is Avogadro's constant and k is Boltzmann's constant.

found throughout thermodynamics. It is also of considerable practical utility for calculating the properties of a perfect gas under a variety of conditions. For instance, the molar volume, $V_m = V/n$, of a perfect gas under the conditions called **standard ambient temperature and pressure** (SATP), defined as 298.15 K and 1 bar, is calculated as 24.789 dm³ mol⁻¹. An earlier definition, **standard temperature and pressure** (STP), was 0 °C and 1 atm; at STP, the molar volume of a perfect gas under these conditions is 22.414 dm³ mol⁻¹.

1A.2(c) Mixtures of gases

When dealing with gaseous mixtures, it is often necessary to know the contribution that each component makes to the total pressure of the sample. The **partial pressure**, p_J , of a gas J in a mixture (any gas, not just a perfect gas), is defined as

$$p_J = x_J p \quad \text{Partial pressure [definition]} \quad (1A.6)$$

where x_J is the **mole fraction** of the component J, the amount of J expressed as a fraction of the total amount of molecules, n , in the sample:

$$x_J = \frac{n_J}{n} \quad n = n_A + n_B + \dots \quad \text{Mole fraction [definition]} \quad (1A.7)$$

When no J molecules are present, $x_J = 0$; when only J molecules are present, $x_J = 1$. It follows from the definition of x_J that, whatever the composition of the mixture, $x_A + x_B + \dots = 1$ and therefore that the sum of the partial pressures is equal to the total pressure:

$$p_A + p_B + \dots = (x_A + x_B + \dots)p = p \quad (1A.8)$$

This relation is true for both real and perfect gases.

When all the gases are perfect, the partial pressure as defined in eqn 1A.6 is also the pressure that each gas would exert if it occupied the same container alone at the same temperature. The latter is the original meaning of 'partial pressure'. That identification was the basis of the original formulation of **Dalton's law**:

The pressure exerted by a mixture of gases is the sum of the pressures that each one would exert if it occupied the container alone.

This law is valid only for mixtures of perfect gases, so it is not used to define partial pressure. Partial pressure is defined by eqn 1A.6, which is valid for all gases.

Example 1A.3 Calculating partial pressures

The mass percentage composition of dry air at sea level is approximately N₂: 75.5; O₂: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.20 atm?

Collect your thoughts Partial pressures are defined by eqn 1A.6. To use the equation, first calculate the mole fractions of the components by using eqn 1A.7 and the fact that the amount of atoms or molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J/M_J$. The mole fractions are independent of the total mass of the sample, so choose the latter to be exactly 100 g (which makes the conversion from mass percentages very straightforward). Thus, the mass of N₂ present is 75.5 per cent of 100 g, which is 75.5 g.

The solution The amounts of each type of atom or molecule present in 100 g of air, in which the masses of N₂, O₂, and Ar are 75.5 g, 23.2 g, and 1.3 g, respectively, are

$$n(\text{N}_2) = \frac{75.5 \text{ g}}{28.02 \text{ g mol}^{-1}} = \frac{75.5}{28.02} \text{ mol} = 2.69 \text{ mol}$$

$$n(\text{O}_2) = \frac{23.2 \text{ g}}{32.00 \text{ g mol}^{-1}} = \frac{23.2}{32.00} \text{ mol} = 0.725 \text{ mol}$$

$$n(\text{Ar}) = \frac{1.3 \text{ g}}{39.95 \text{ g mol}^{-1}} = \frac{1.3}{39.95} \text{ mol} = 0.033 \text{ mol}$$

The total is 3.45 mol. The mole fractions are obtained by dividing each of the above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.20 atm):

	N ₂	O ₂	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.936	0.252	0.012

Self-test 1A.3 When carbon dioxide is taken into account, the mass percentages are 75.52 (N₂), 23.15 (O₂), 1.28 (Ar), and 0.046 (CO₂). What are the partial pressures when the total pressure is 0.900 atm?

Answer: 0.703, 0.189, 0.0084, and 0.00027 atm

Exercises

E1A.3 Could 131 g of xenon gas in a vessel of volume 1.0 dm³ exert a pressure of 20 atm at 25 °C if it behaved as a perfect gas? If not, what pressure would it exert?

E1A.4 A perfect gas undergoes isothermal compression, which reduces its volume by 2.20 dm³. The final pressure and volume of the gas are 5.04 bar and 4.65 dm³, respectively. Calculate the original pressure of the gas in (i) bar, (ii) atm.

E1A.5 At 500 °C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m⁻³. What is the molecular formula of sulfur under these conditions?